2-Methyl-2-propionylmethyl-5,6-dihydro-7H-pyrrolo[2,1-b]oxazolinium Perchlorate (Vc). N-Methallylpyrrolidone Ig (2.8 g, 20 mmole) was dissolved in 25 ml propionic anhydride and 2 ml 70% $HClO_4$ was added. The mixture was allowed to stand overnight, then treated with 200 ml ether, and the resulting oil was dissolved in 3 ml isopropyl alcohol and cooled to 0°C. The salt precipitated out and was filtered and washed with a small amount of isopropyl alcohol and then ether, and dried. Yield 1.5 g (25%).

N-(4-Oxo-2-methylpenten-2-yl-1)naphthalimide (VI). Salt Va was treated with a 5% NaOH solution in aqueous methanol. The resulting white precipitate was filtered, washed with water, and dried, then recrystallized from benzene. Quantitative yield.

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CONDENSED THIOLANE 1,1-DIOXIDE SYSTEMS.

3.* TWO MODES OF CYCLIZATION OF N-SUBSTITUTED trans-3-CHLORO-4-THIOUREIDOTHIOLANE 1,1-DIOXIDES

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UDC 547.789.61'785.5'732.07:541.124

Reaction of trans-3-chloro-4-aminothiolane 1,1-dioxide hydrochloride with aryl isothiocyanates gives, according to the base involved, cis-perhydrothieno[3,4-d]imidazole-2-thione 5,5-dioxides or the hitherto undescribed cis-2-arylimino-perhydrothieno[3,4-d]thiazole 5,5-dioxides.

Two principal methods are known for the synthesis of cis-fused bicylic systems containing the thiolane 1,1-dioxide ring, namely from cis-bifunctionally substituted thiolane 1,1-dioxides [2, 3], or by intramolecular cyclization of 4-substituted 2-thiolene 1,1-dioxides [4-6]. The latter can be obtained, for example, by elimination, a reaction which has been well studied in the thiolane 1,1-dioxide series [7, 8]. A third possible route for the cyclization to give cis-fused systems, nucleophilic substitution by the S_N2 mechanism, has not hitherto been realized in the thiolane 1,1-dioxide series.

We have found that trans-3-chloro-4-aminothiolane 1,1-dioxide hydrochloride (I) reacts with aryl isothiocyanates in the presence of strong bases (triethylamine, aqueous sodium carbonate) to give the known cis-perhydrothieno[3,4-d]imidazole-2-thione 5,5-dioxides (IIIa-c) [5, 9]. The use of less basic tertiary amines (pyridine or N,N-dimethylaniline) facili-

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*For Part 2, see [1].
†Deceased.

Department of Petroleum Chemistry, Institute of Physical Organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252160. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1420-1423, October, 1988. Original article submitted March 26, 1987; revision submitted February 26, 1988.

0009-3122/88/2410-1180$12.50

TABLE 1. Properties of Compounds Obtained

Compound	mp, °C (solvent)	Found, %			Empirical formula	Calculated, %			IR spectrum, cm^{-1}	Yield, %
		Hal	N	S		Hal	N	S		
IIIa	277 (dioxane)	—	10,5	23,8	$C_{11}H_{12}N_2O_2S_2$	—	10,4	23,9	3160, 1505, 1310, 1110	82
IIIb	250 (dioxane)		8,2	18,1	$C_{11}H_{11}BrN_2O_2S_2$	—	8,1	18,4	3200, 1500, 1320, 1120	70
IIIc	230 (alcohol)	—	7,9	18,2	$C_{11}H_{11}BrN_2O_2S_2$	—	8,1	18,4	3200, 1510, 1320, 1120	62
IVa*	192 (alcohol–water)	11,5	9,1	20,8	$C_{11}H_{13}ClN_2O_2S_2$	11,6	9,2	21,0	3200, 1630, 1300, 1130	92
IVb*	179 (alcohol–water)	—	7,6	16,4	$C_{11}H_{12}ClBrN_2O_2S_2$	—	7,3	16,7	3520, 3370, 1680, 1335, 1155	75
IVc	209 (acetonitrile)	23,5	—	18,2	$C_{11}H_{11}BrN_2O_2S_2$	23,0	—	18,4	3370, 1680, 1325, 1140	80
IVd	210 (alcohol)	20,9	8,3	19,0	$C_{11}H_{10}Cl_2N_2O_2S_2$	21,0	8,3	19,0	3120, 1660, 1320, 1120	59
IVe	226 (alcohol)	—	9,7	21,5	$C_{12}H_{12}N_2O_3S_2$	—	9,5	21,7	3230, 1620, 1340, 1130	90
IVf*	240 (alcohol–water)	15,7	—	28,3	$C_5H_9ClN_2O_2S_2$	15,5	—	28,0	3300, 1640, 1300, 1100	80
IIe	234 (alcohol)	10,8	8,5	19,4	$C_{12}H_{13}ClN_2O_3S_2$	10,7	8,4	19,3	3330, 1320, 1120	78

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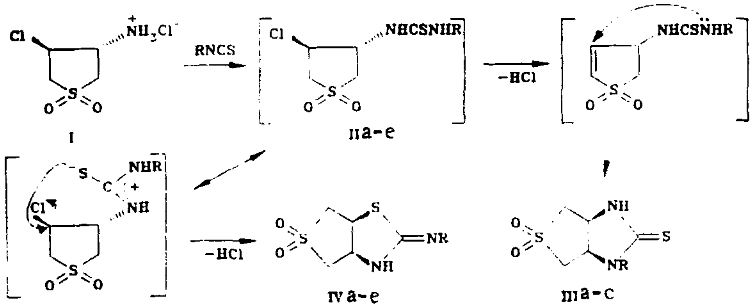
*The compounds are isolated and identified as their hydrochlorides.

TABLE 2. ^{13}C NMR Spectral Data for cis-2-Iminoperhydrothieno[3,4-d]thiazole 5,5-Dioxides (IVa-d) and the Model Compounds (Va, d) and (VIa, d)

Compound	Chemical shifts, ppm								
	$C_{(2)}$	$C_{(3a)}$	$C_{(4)}$	$C_{(6)}$	$C_{(6a)}$	$C_{(1')}$	$C_{(2')}$, $C_{(6')}$	$C_{(3')}$, $C_{(5')}$	$C_{(4')}$
IVa	154,27	73,06*	55,98	54,93	45,98	141,17*	117,99	128.50	121.74
IVb	152,37*	65,14	53,95	52,83	44,07*	138,52*	117,99	129.29	111.19
IVc**	158,50	60,05*	55,57	55,03	43,42*	147,18*	128,02 123,33	124,54 132,33	116.75
IVd	160,76	58,27*	55,60	55,20	43,94*	145,10*	127,75	128.18	124.38
Va	—	—	—	—	—	—	—	—	122,6
Vd	—	—	—	—	—	146.8	128,3	128.0	123.6
VIa	—	—	—	—	—	—	—	—	125,0
VId	—	—	—	—	—	140,5	136,5	128.7	129,6

*Signals broadened.
**Assignment of the ^{13}C signals for the aromatic ring is provisional.

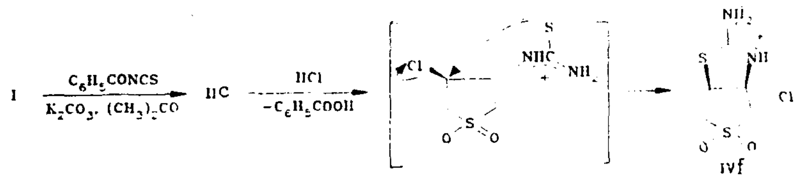
tates the formation of the novel cis-aryliminoperhydrothieno[3,4-d]thiazole 5,5-dioxides (IVa-d). It may be assumed that strong bases accelerate the elimination of hydrogen halide, whereas use of the more weakly basic tertiary amines results in nucleophilic replacement becoming predominant:



II—IV a $R=C_6H_5$; b $R=p\text{-}BrC_6H_4$; c $R=o\text{-}BrC_6H_4$; d $R=2.6\text{-}Cl_2C_6H_3$; e $R=COC_6H_5$

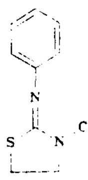
In the case of benzoyl isothiocyanate, the course of the reaction is independent of the tertiary amine used. Only the thiazolidine (IVe) is formed, evidently as a result of the reduced nucleophilicity of the nitrogen atom attached to the benzoyl group.

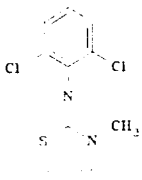
The intermediate (IIe) can be isolated when the reaction is carried out in dry acetone in the presence of calcined potassium carbonate. When the reaction is carried out in protic solvents, the sulfone (IIe) is converted quantitatively into the thiazolidine (IVe). Acid hydrolysis of (IIe) gives the thiazolidine (IVf) [9].

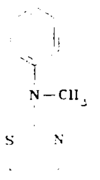


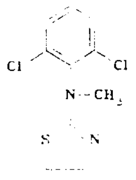
The cis-structure of the products of intramolecular cyclization of 4-substituted 2-thiolene 1,1-dioxides has been discussed on more than one occasion [3-6]. It appears that reaction of thioureas (IIa-e) by the S_N2 mechanism also results in cis-fusion of the rings.

There has been much discussion in the literature on amino-imino tautomerism in arylaminothiazolidines [10-12]. The shift in the C=O absorption in the IR spectrum of (IVe) (1620 cm^{-1}, Table 1) indicates that the imino-tautomer predominates [13, 14]. Comparison of the chemical shifts of the aromatic ring carbons in the ^{13}C NMR spectra of bases (IVa) and (IVe) (Table 2) with analogous data for the model heterocycles (Va, d) and (VIa, d) [15, 16]


Va


Vd


VIa


VId

also enables the imino-structure to be assigned to the bicyclic compounds (IV). However, a final decision as to the structure of (IV) requires examination of the ^{15}N NMR spectra of the isotope-enriched compounds. In addition, further examination requires an anomalously great range (14.8 ppm) of chemical shifts for the $C_{(3a)}$ carbon (attached to nitrogen) and broadening of some of the signals in the $^{13}C\ \{^1H\}$ spectrum (Table 2).

EXPERIMENTAL

IR spectra were obtained on a UR-20 in KBr disks. $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker WP-200 spectrometer with an operating frequency for ^{13}C nuclei of 50.33 MHz, in DMSO-D_6 at 295°K. Chemical shifts were measured relative to TMS as internal standard. Assignment of the signals was made from spectra with partial decoupling from protons.

cis-1-Phenylperhydrothieno[3,4-d]imidazole-2-thione 5,5-Dioxide (IIIa). To 2.06 g (0.01 mole) of (I) hydrochloride in 50 ml of alcohol was added 1.35 g (0.01 mole) of phenyl isothiocyanate and 5.05 g (0.05 mole) of triethylamine. The solution was boiled for 30 min with stirring, cooled, and the solid which separated was washed with water (50 ml), alcohol (30 ml), and ether (50 ml). Yield 2.20 g. Thioureas (IIIb) and (IIIc) were obtained similarly from (I) hydrochloride and the isothiocyanates in the presence of triethylamine or aqueous sodium carbonate (Table 1).

2-Phenylamino-cis-perhydrothieno[3,4-d]thiazole 5,5-Dioxide Hydrochloride (IVa). To 2.06 g (0.01 mole) of the salt (I) in 50 ml of ethanol was added 1.35 g (0.01 mole) of phenyl isothiocyanate and 7.90 g (0.10 mole) of pyridine. The solution was boiled for 30 min, and the solid which separated was filtered off, washed with alcohol (30 ml), ether (20 ml), and crystallized from 70% aqueous alcohol. Yield 2.80 g. Similarly, from hydrochloride (I) and the isothiocyanates in the presence of pyridine there were obtained (IVb-d). The sulfone (IVe) was obtained in 54% yield under these conditions. The use of triethylamine or sodium carbonate as base gave the sulfone (IVe) in yields of 90 and 34% respectively. Compounds (IVa) and (IVb) were isolated from the reaction mixture as their hydrochlorides, and (IVc-e) as the free bases.

2-Imino-cis-perhydrothieno[3,4-d]thiazole 5,5-Dioxide Hydrochloride (IVf). A. A mixture of 6.60 g (0.02 mole) of the thiourea (IIe) in 80 ml of conc. hydrochloric acid and 20 ml of water was boiled until the starting sulfone had dissolved completely. The mixture was then evaporated to dryness, and the residue washed with alcohol and ether (20 ml of each) and crystallized from 90% aqueous ethanol. Yield 3.65 g..

B. Obtained by hydrolysis of (IVe) in 30% aqueous hydrochloric acid. Yield 93%.

trans-3-(3'-Benzoylthioureido)-4-chlorothiolane 1,1-Dioxide (IIe). To 10.3 g (0.05 mole) of the hydrochloride (I) in 100 ml of dry acetone was added a solution of 0.07 mole of benzoyl isothiocyanate in 35 ml of dry acetone and 3.5 g of calcined potassium carbonate. The mixture was boiled for 3 h with vigorous stirring, and the solid which separated was washed with water (3 × 100 ml), acetone (50 ml), and ether (100 ml). Crystallization from ethanol gave 13.0 g of product (Table 1).

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